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The influence of chain stretching on the phase behavior of multiblock copolymer and comb copolymer melts

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Abstract. The subject of this paper is inspired by microphase-separated copolymer melts in which a small-scale structure is present inside one of the phases of a large-scale structure. Such a situation can arise in a diblock copolymer melt, if one of the blocks of the diblock is in itself a multiblock copolymer or a comb copolymer. Due to the presence of the large-scale structure, the chains are stretched. The aim of this paper is to investigate the influence of this chain stretching on the formation of the small-scale structure. To gain insight we study infinite melts of infinitely long copolymer chains that are subjected to a stretching force. For melts of monodisperse multiblock copolymers we find that the stretching destabilizes the homogeneous phase. If the stretching is strong, the lamellar structure is the only stable structure. The periodicity increases with the degree of stretching. For melts of monodisperse comb copolymers the chain stretching has no influence on the stability of the homogeneous phase. If the stretching is strong, the lamellar structure and the hexagonal structure are the only stable structures. The periodicity is independent of the degree of stretching. For the multiblock copolymer we investigated the influence of block length polydispersity. For small polydispersity the period of the structure increases monotonically with the degree of stretching. For intermediate polydispersity, the period initially *decreases* before it starts to increase. For large polydispersity, the mean-field period at the spinodal is infinite, becoming finite once the stretching force exceeds some critical value. For very large polydispersity the mean-field period at the spinodal remains infinite for any value of the stretching force.

PACS. 82.35.Jk Copolymers, phase transitions, structure – 89.75.Fb Structures and organization in complex systems – 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling

1 Introduction: Microphase separation at two length scales

The subject of this paper is inspired by microphase-separated copolymer melts in which a small-scale structure is present inside one of the phases of a large-scale structure. There are several copolymer architectures that give rise to such a complicated microstructure. An example is a diblock copolymer where one of the blocks is a homopolymer with monomers of type C, while the other block is either a comb copolymer with monomers of types A and B, or a multiblock copolymer with monomers of types A and B, see Figure 1 for illustration. When the temperature is lowered starting from the homogeneous phase, a transition to a microphase-separated state may occur. Most likely this transition will separate the C-monomers from the A- and B-monomers, leading to a microstructure characterized by a large length scale. When the temperature is lowered further, a second phase transition may occur, one that will separate the A-monomers from the B-monomers. This will lead to a small-scale structure inside the copolymeric phase of the large-scale structure (see Fig. 2; electron microscope image). An interesting possibility that has attracted a lot of attention lately [1–4] is to attach the side chains of the comb copolymer block to the backbone by means of reversible hydrogen bonds.

The second-order vertex function (which gives information about the position of the spinodal and about the weak-segregation periodicity) has already been calculated in the situation where the homopolymer block is chemically identical to one of the species of the copolymer block [5,6]. It was shown that under certain conditions the vertex function has two minima. One of these corresponds to the separation of the homopolymer block from the copolymer block (large length scale), while the other corresponds to the separation inside the copolymer block (small length scale). If both minima are present, the two

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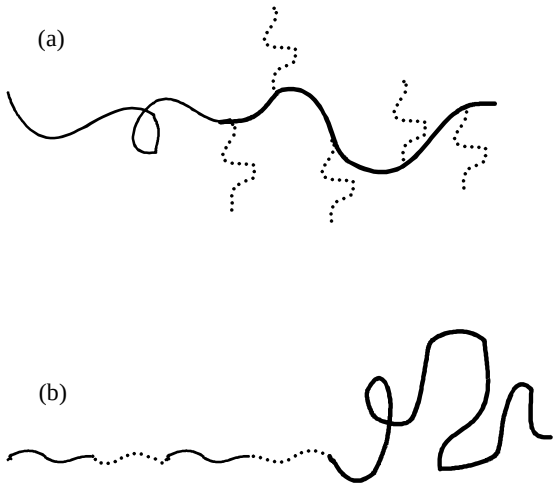

Fig. 1. Schematic picture of a diblock copolymer consisting of a homopolymer block and either a comb copolymer block (a) or a multiblock copolymer block (b). A melt consisting of such molecules can have a microstructure with two length scales.

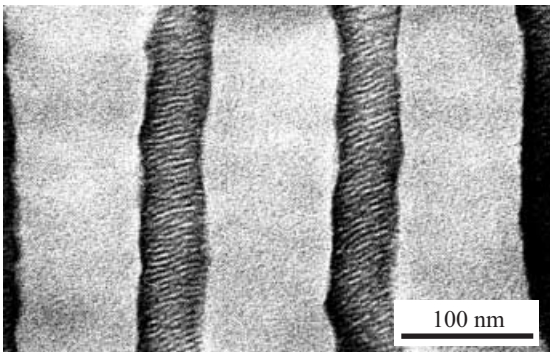

Fig. 2. Experimental example of a two–length-scale microstructure for a comb-coil diblock copolymer consisting of a supramolecular comb copolymer block P4VP(PDP), obtained by hydrogen bonding of pentadecylphenol (PDP) to poly(4-vinylpyridine) (P4VP), and a homopolymer block of polystyrene. Courtesy of Janne Ruokolainen (from Ref. [2]).

microstructures will be formed more or less simultaneously, leading to interesting problems concerning interference and commensurability.

In the present paper we consider quite a different regime, namely, the regime where the large-scale structure is already fully formed when the small-scale structure arises. We will also assume that the ratio between the two length scales is large. The presence of the strongly segregated large-scale structure will cause the chains to be stretched. We are interested in the influence of this chain stretching on the formation of the small-scale structure. The degree of chain stretching will vary within the domains of the large-scale structure. Nevertheless, if the period of the large-scale structure is much larger than the period of the small-scale structure, the degree of stretching is more or less constant across several periods of the small-scale structure. In this situation, the local small-scale structure may be found by considering a melt of infinitely long copolymer chains, each of which is subjected to the same stretching force working on its end points.

An important question is whether experimentally the degree of stretching is a free parameter that can be chosen at will. The answer is affirmative: the degree of stretching can be tuned by varying the total degree of polymerization, keeping the local architecture of the copolymeric part the same. The larger the degree of polymerization, the weaker the stretching. This statement can be verified in the following way. In the strong-segregation regime, the period L of the microstructure varies with the degree of polymerization N as $L \propto aN^{2/3}$, where a is the statistical segment length. This implies that the chains are stretched [7]. A stretched chain can be visualized as a linear array of Gaussian blobs, each containing g-monomers. The number of blobs is equal to N/g, while the size of one blob is equal to $ag^{1/2}$. We can now determine g via

$$\frac{N}{g} a g^{1/2} \cong L \cong a N^{2/3} \quad \Rightarrow \quad g \cong N^{2/3} \,. \tag{1}$$

Equation (1) shows that the blobs become larger when N increases, and larger blobs imply weaker stretching. By making the molecules long enough, the degree of stretching can be made arbitrarily small. Weak stretching will be defined by the condition that one blob contains more than one repeating unit of the comb copolymer or the multiblock copolymer, where a repeating unit is defined as an A-block plus a B-block in case of a multiblock copolymer, and as a side chain plus the corresponding piece of the backbone in case of a comb copolymer.

2 Mono-disperse case

Much about the phase behavior can already be deduced from the second-order vertex function $\Gamma(\vec{q})$ [8,9]. It has two important characteristics: its minimum value $2\chi_{\rm s}$, and the set of vectors $\vec{q}$ for which $\Gamma(\vec{q}) = 2\chi_{\rm s}$. In case there is no stretching force, this set has the shape of a spherical shell that can be fully characterized by its radius q_0. Both $\chi_{\rm s}$, and q_0 have physical interpretations: $\chi_{\rm s}$ is the spinodal value of the χ-parameter, and $2\pi/q_0$ is very close to the period of the weakly segregated microstructure. If a stretching force $\vec{F}$ is applied, the spherical symmetry is broken, but the vertex function will remain symmetric with respect to rotations around the direction of the force. This means that one can write $\Gamma(\vec{q}) = \Gamma(q, \theta)$, where q is the length of $\vec{q}$, and θ is the angle between $\vec{F}$ and $\vec{q}$. In the Appendix it is shown how $\Gamma(q, \theta)$ can be calculated for a multiblock copolymer melt for general block length distributions; see references [10–12] for the calculation of the second-, third- and fourth-order vertex functions in the absence of a stretching force. Appendix A shows that $\Gamma(q, \theta)$ depends on θ only through the combination $F \cos\theta$. This means that for $\vec{q}$-vectors that are perpendicular to $\vec{F}$, the vertex function has the same value as in the absence of chain stretching. We will use this important feature later on in the calculation of the phase diagram of the comb copolymer melt.

2.1 Multiblock copolymers

We will consider first a melt of monodisperse multiblock copolymers. Calculations show that in the presence of a stretching force, the second-order vertex function looses its spherical symmetry and attains its absolute minimum in two discrete points $\pm\vec{q}_0$ in Fourier space. This means that if the χ-parameter is gradually increased from zero, the homogeneous melt starts loosing its stability only with respect to two Fourier modes $\psi(\vec{q}_0)$ and $\psi(-\vec{q}_0)$. When the stretching is strong enough, these minima are deep, and the only stable structure will be the lamellar structure, because any other structure involves Fourier modes with respect to which the system is still stable. This means that it is not necessary to calculate the higher-order vertices in order to conclude that the lamellar structure has a lower free energy than the other structures. This situation is to be contrasted with the situation in the absence of chain stretching, when the homogenous melt looses stability simultaneously with respect to *all* Fourier modes lying in a spherical shell. In that case, all structures are equivalent up to second order in the free-energy expansion, and higher-order vertices have to be calculated in order to find out which structure is stable. In this respect, the presence of chain stretching simplifies matters.

The location of the spinodal in the (f, χ)-plane (where f is the composition, *i.e.* the fraction of monomers of type A) is determined by the minimum value of the vertex function. It turns out that if the strength of the stretching force increases, the minimum of the vertex function decreases, meaning that the spinodal shifts downwards in the (f, χ)-plane. In other words, the stretching destabilizes the homogeneous phase. In order to find the exact location of the binodal corresponding to the transition from the homogeneous phase to the lamellar phase, we would have to calculate the vertex functions up to fourth order. However, we believe that it would not be worthwhile to delve into these calculations, because the difference between the calculated binodal and the calculated spinodal would be much smaller than the difference between the calculated binodal and the experimental binodal. This is because the model used in this paper is a qualitative model, aimed at providing a description on a coarse-grained level only. Therefore, we did not calculate the binodal, and in Figure 3b we used the spinodal as an approximation to the binodal. The calculation has been done for $\tilde{F}^2 \equiv NF^2 = 1$, where N is the number of monomers in one repeating unit of the multiblock (= A-block plus B-block). For this choice of F, one blob of the stretched chain contains roughly one repeating unit. Figure 3a presents the phase diagram in the absence of stretching. It has been calculated using all vertices up to the fourth order. For the calculation of these vertices we refer to [10–12]. The main results of our analysis of the monodisperse multiblock copolymer melt are that chain stretching has the following effects:

- The binodal shifts downwards in the (f, χ)-plane,
- When the force is sufficiently strong, only the lamellar structure is stable,
- The period of the microstructure increases with increasing chain stretching.

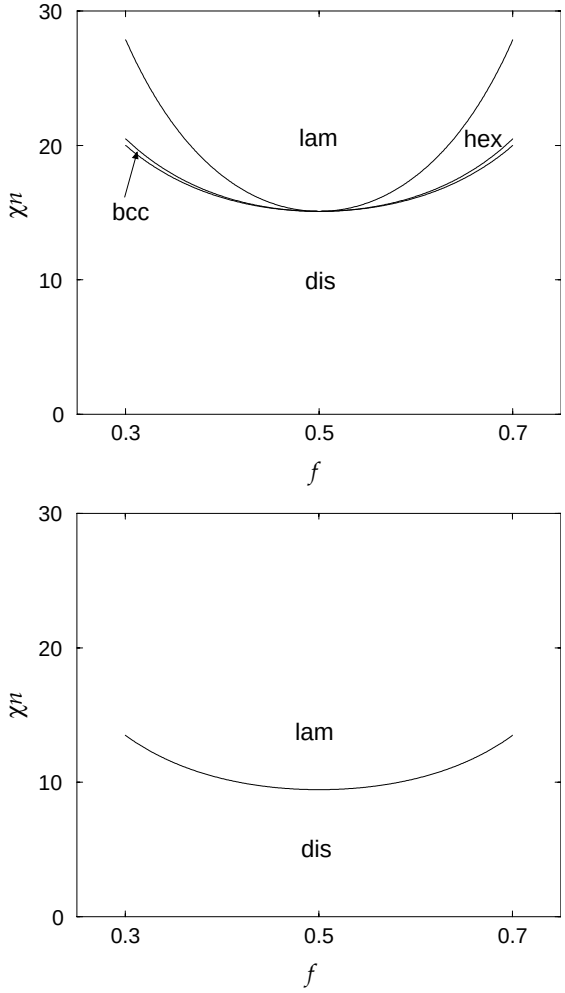

Fig. 3. a) Phase diagram of a multiblock copolymer in the absence of chain stretching. b) Phase diagram of multiblock copolymer in the presence of chain stretching, for $\tilde{F} = 1$. All phases other than lamellar disappear. The binodal has been approximated by the spinodal. Horizontal: A-monomer fraction. Vertical: χ-parameter multiplied by the average number of monomers per block.

2.2 Comb copolymers

We will contrast the phase behavior of monodisperse multiblock copolymer melts with that of monodisperse comb copolymer melts. Also in this case the second-order vertex function $\Gamma(\vec{q})$ looses its spherical symmetry in the presence of chain stretching. The vertex attains its minimum on a circle in Fourier space. The radius of this circle is independent of the degree of the stretching, while the plane of the circle is perpendicular to the direction of the stretching. When the χ-parameter is gradually increased from zero, the homogeneous melt becomes unstable with respect to the formation of microstructures whose lattice vectors lie on this circle. Such structures are either one-, or two-dimensional. Making use of experience with weak-segregation melts in the absence of chain stretching, we choose to consider only the lamellar structure and the hexagonal structure. In order for the lattice vectors to lie

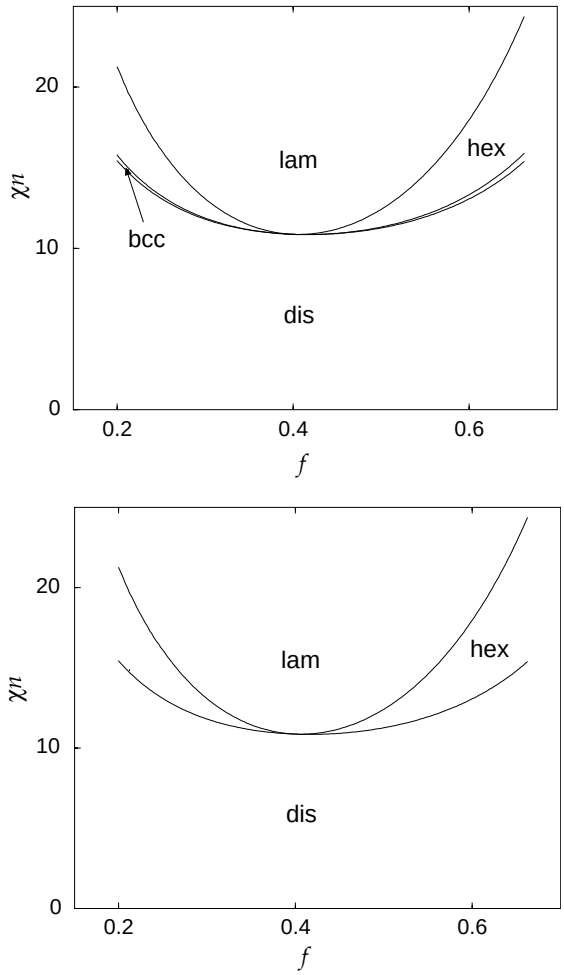

Fig. 4. a) Phase diagram of comb copolymer in the absence of chain stretching. b) Phase diagram of comb copolymer in the presence of chain stretching. Horizontal: A-monomer fraction. Vertical: χ-parameter multiplied by the average number of monomers per repeating unit. Figures provided by Rikkert Nap.

on the above-mentioned circle, the structures have to be oriented. The lamellas of the lamellar structure, and the cylinders of the hexagonal structure, have to be parallel to the direction of stretching. In order to draw the phase diagram, we need the vertices up to the fourth order. Calculating the general expressions for the higher-order vertices in the presence of chain stretching would be a formidable task, because we cannot make use of spherical symmetry anymore. Luckily, we need not calculate these general expressions in order to be able to draw the phase diagram. This is due to the fact that if all Fourier vectors $\vec{q}_1$, $\vec{q}_2$, $\ldots$, $\vec{q}_n$ are perpendicular to the direction of stretching, then $\Gamma(\vec{q}_1, \vec{q}_2, \ldots, \vec{q}_n)$ is the same as it would be in the stretch-free case (see App. A). Since all Fourier modes of the oriented lamellar and the oriented hexagonal structure are perpendicular to the direction of stretching, the free energy of the oriented lamellar phase and the free energy of the oriented hexagonal phase can be calculated using the vertices of the stretch-free case. These vertices have been calculated in [6], and making use of these results we arrived at the phase diagrams shown in Figures 4a and b.

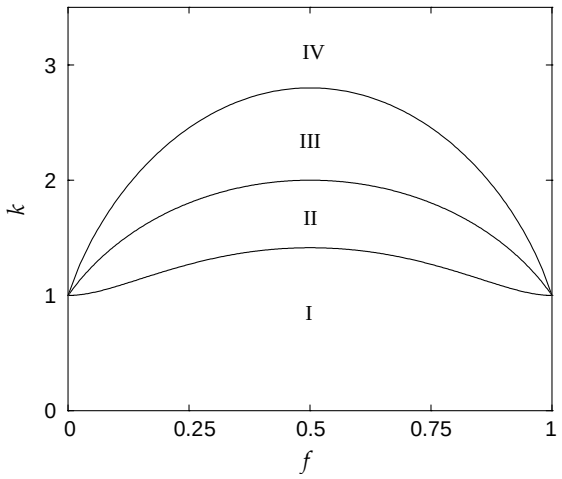

Fig. 5. Curves delineating regions of different behavior of the position of the minimum of the scattering function with increasing degree of stretching. The classification of the regions I, II, III and IV has been given in the text.

3 Polydisperse multiblock copolymer

Next, we consider the influence of chain stretching on the phase behavior of melts of *polydisperse* multiblock copolymers. We study the situation where both the A-blocks, and the B-blocks have a Schultz-Zimm distribution [10, 12]. This distribution is defined in equation (A.15) of the Appendix. It has two independent parameters by which both the mean, and the standard deviation can be chosen independently. In the calculations we assumed that the A- and B-blocks have the same polydispersity. The results will be presented in the (f, k)-plane, where f is the fraction of A-monomers, and k is the inverse polydispersity, defined by

$$\frac{1}{k} = \frac{n_{\mathrm{w}}}{n_{\mathrm{n}}} - 1. \tag{2}$$

Here n_{n}, n_{w} denote the number and weight average chain lengths. First, we consider the situation where no stretching force is present. In the region defined by

$$k \leqslant \sqrt{1 + 12f - 12f^2} \tag{3}$$

the vertex function attains its minimum at $q_0 = 0$ (see, *e.g.*, [10]). In Figure 5, this region corresponds to regions I and II combined. In regions III and IV, the vertex function attains its minimum at $q_0 > 0$. When in Figure 5 the value of k is increased for a fixed value of f, then starting from region III the value of q_0 increases monotonically, and reaches a finite value in the monodisperse limit $k \to \infty$.

Stretching the chains can change both q_0 and χ_{s} (remember that these parameters refer to the absolute minimum of $\Gamma(\vec{q})$). In order to find out whether it is possible

that q_0 becomes non-zero in regions I or II, or that it becomes zero in regions III or IV, we calculated the slope of $\Gamma(q,\theta)$ at the origin. The result is

$$\left.\frac{\partial\Gamma(q,\theta)}{\partial(q^2)}\right|_{q=0} = \frac{1}{4x} - \frac{k^2-1}{48x^2} + \frac{1+2x+24x^2-(1+2x)\,k^2}{24kx^2}\;\tilde{F}^2\cos^2\theta\,. \tag{4}$$

Here we have defined

$$x = f(1-f)\,, \tag{5}$$

$$\tilde{F}^2 = \frac{\bar{n}}{6}\left(\frac{Fa}{k_{\rm B}T}\right)^2 = \bar{n}F^2\,, \tag{6}$$

$$\bar{n} = n_A + n_B \tag{7}$$

with n_α the average length of blocks of type $\alpha = A, B$. In equation (6) we used our special choice for the units of length and energy (see App. A). Note that $\tilde{F}$ is the stretching force in natural units: when $\tilde{F} = 1$, each blob of the stretched chain contains roughly one block of the multiblock. The important property is the sign of the coefficient c of $\tilde{F}^2$ in equation (4). In region I we have $c > 0$. This means that in this region, q_0 will stay zero for all $\tilde{F}$. Since $\Gamma(q=0)$ is independent of $\tilde{F}$, we can deduce that in region I the position of the spinodal is independent of $\tilde{F}$. In region II, $q_0 = 0$ when $\tilde{F} = 0$, but since $c < 0$, q_0 will deviate from zero, and the spinodal value of the χ-parameter will decrease, once $\tilde{F}$ exceeds some critical value. In regions III and IV, $q_0 > 0$ when $\tilde{F} = 0$. Since in these regions $c < 0$, we conclude that $q_0 > 0$ for all $\tilde{F}$. One can show that the spinodal value of χ decreases with increasing $\tilde{F}$, *i.e.* the chain stretching destabilizes the system. A very interesting property of region III is that on increasing $\tilde{F}$ from zero, the periodicity q_0^{-1} of the system *decreases* first, before it starts to increase again at larger values for $\tilde{F}$. Unfortunately, we have not been able to find an intuitive, convincing reason why this should be the case. In region IV, the periodicity increases with $\tilde{F}$ for all values of $\tilde{F}$.

4 Suggestion for further research

An interesting and much studied copolymer system is the correlated random copolymer (see, for instance, [10]). The block lengths of a random copolymer have an exponential distribution, which is equivalent to a Zimm-Schultz distribution with $k = 1$, and arbitrary $0 < f < 1$. Judging from Figure 5, all random copolymers belong to region I. This means that $q_0 = 0$ for any value of the stretching force $\tilde{F}$, and that the spinodal does not shift. In order to find the influence of stretching on the microstructure periodicity, the so-called non-local contribution to the free energy has to be calculated. This would be an interesting exercise, because it is not obvious beforehand whether the periodicity would increase or decrease.

The authors thank Janne Ruokolainen for providing Figure 2 (cf. Ref. [2]), and R. Nap for providing Figures 4a and b.

Appendix A. The second-order vertex function

Consider the bead-spring model of a polymer chain. A stretching force $\vec{F}$ working on the end points of the chain can be incorporated by adding a factor $\exp(\vec{F}\cdot\vec{r}/kT)$ to the single-bond distribution function. If the Fourier transform of the single-bond distribution function in the absence of a force is given by [13]

$$g_0(\vec{q}) = e^{-a^2q^2/6}\,, \tag{A.1}$$

where the statistical segment length a is a measure for the average distance between two consecutive monomers along the chain, then the normalized Fourier transform of the single-bond distribution function in the presence of a force is given by

$$g(\vec{q}) = e^{-a^2\left(q^2-2i\vec{F}\cdot\vec{q}/kT\right)/6}\,. \tag{A.2}$$

Adopting units in which $kT = 1$ and $a^2 = 6$, and denoting the angle between $\vec{F}$ and $\vec{q}$ by θ, we obtain

$$g(\vec{q}) = e^{-(q^2-2iFq\cos\theta)}\,. \tag{A.3}$$

The single-bond distribution function $g(\vec{q})$ is the basic building block for the calculation of the correlation functions, which are needed to find expressions for the vertex functions. For a polydisperse copolymer melt containing two monomer types A and B, the second-order vertex function is given by

$$\gamma(\vec{q}) = \frac{\mathrm{g}_{AA}(\vec{q})+\mathrm{g}_{AB}(\vec{q})+\mathrm{g}_{BA}(\vec{q})+\mathrm{g}_{BB}(\vec{q})}{\mathrm{g}_{AA}(\vec{q})\mathrm{g}_{BB}(\vec{q})-\mathrm{g}_{AB}(\vec{q})\mathrm{g}_{BA}(\vec{q})} - 2\chi. \tag{A.4}$$

In order to define the correlation functions $\mathrm{g}_{\alpha\beta}(\vec{q})$, where α and β are variables taking on the values A or B, we need first some definitions. Let s denote a molecule type (that is, an ordered sequence of A's and B's), and let N_s be the number of monomers in a molecule of type s. Let ρ_s be proportional to the total number of molecules of type s in the melt, normalized in such a way that $\sum \rho_s N_s = 1$. Define the function σ_{si}^{α} in the following way: $\sigma_{si}^{\alpha} = 1$ if the i-th monomer in a molecule of type s is of type α, and $\sigma_{si}^{\alpha} = 0$ otherwise. Using these definitions, the correlation functions $\mathrm{g}_{\alpha\beta}(\vec{q})$ can be written as follows:

$$\mathrm{g}_{\alpha\beta}(\vec{q}) = \sum_s \rho_s \mathrm{g}^s_{\alpha\beta}(\vec{q})\,, \qquad \mathrm{g}^s_{\alpha\beta}(\vec{q}) = \sum_{i,j=1}^{N_s} \sigma_{si}^{\alpha}\sigma_{sj}^{\beta}\mathrm{g}_{ij}(\vec{q}) \tag{A.5}$$

$$\begin{aligned} &\mathrm{g}_{ij}(\vec{q}) = g(\vec{q})^{j-i}\,, && \text{if } i<j\,,\\ &\mathrm{g}_{ij}(\vec{q}) = g(\vec{q})^{i-j} = g^*(-\vec{q})^{i-j}\,, && \text{if } i>j\,. \end{aligned} \tag{A.6}$$

Here * denotes the complex conjugate. Note that in the presence of a stretching force, $g(\vec{q})$ need not be real. It turns out to be convenient to define

$$h_{\alpha\beta}(\vec{q}) = \sum_s \rho_s \sum_{i<j} \sigma_{si}^{\alpha}\sigma_{sj}^{\beta} g^{j-i}(\vec{q})\,, \tag{A.7}$$

so that

$$\mathtt{g}_{\alpha\beta}(\vec{q}) = h_{\alpha\beta}(\vec{q}) + h^*_{\alpha\beta}(\vec{q})\,. \tag{A.8}$$

We wish to calculate the second-order vertex function for a melt of stretched polydisperse AB-multiblock copolymers. Let $Q \gg 1$ be the number of A-blocks in the molecule, which equals the number of B-blocks. Let $P_\alpha(n)$ be the length distribution of the blocks of type α. Let n_i denote the length of the i-th A-block, and m_i the length of the i-th B-block. For this system a molecule type can be specified by giving the lengths of all blocks, that is, $s := \{n_1, n_2, ..., n_Q; m_1, m_2, ..., m_Q\}$. Using the normalization condition $\sum \rho_s N_s = 1$, we find

$$\rho_s = \frac{1}{Q(n_A + n_B)} P_A(n_1)...P_A(n_Q)P_B(m_1)...P_B(m_Q)\,. \tag{A.9}$$

First, we will calculate h_{AA}. The double summation over i and j present in equation (A.7) can be split into two parts, $h^{(1)}_{AA}$ and $h^{(2)}_{AA}$. The first part $h^{(1)}_{AA}$ is defined as the sum over all pairs (i,j), where i and j are present in the same block. Its value can be obtained by restricting the summation to monomers that are both present in the k-th block for arbitrary k, and multiplying the result with Q. It should be noted that this factor Q is cancelled by the factor $1/Q$ present in the normalization constant for ρ_s, see equation (A.9). We obtain

$$h^{(1)}_{AA} = \bar{n}\left(\frac{\alpha_z - 1}{z^2} + \frac{f}{z}\right)\,, \tag{A.10}$$

where f is the fraction of A-monomers in the melt, $\bar{n} = n_A + n_B$, and $n_\alpha = \int \mathrm{d}n P_\alpha(n) n$ is the average number of monomers in a block of type α. The variable z is defined by

$$\begin{aligned} z &= y - 2i\tilde{F}\sqrt{y}\,\cos\theta\,, \\ y &= \bar{n}q^2\,, \\ \tilde{F}^2 &= \bar{n}F^2 \end{aligned} \tag{A.11}$$

and α_z is the Laplace transform of the length distribution of the A-blocks:

$$\alpha_z = \int_0^\infty \mathrm{d}n P_A(n) e^{-\frac{nz}{\bar{n}}}\,. \tag{A.12}$$

Note that the condition of weak stretching, as defined in the introduction, corresponds to $\tilde{F} \ll 1$. To obtain the second contribution $h^{(2)}_{AA}$, the summation is restricted to monomers that are present in different blocks. Generally, the contribution from any pair (i,j) decreases exponentially with the distance $(j-i)$ along the chain, and so the contribution from pairs for which this distance is much larger than q^{-2} is negligible. Since the relevant q-values are determined by the block length distributions and not by the total number of blocks, it follows that for large Q the monomers have to be relatively close together in order to give a non-negligible contribution to the summation. Consequently, the main part of $h^{(2)}_{AA}$ is proportional to Q, and not to Q^2, despite the presence of the double summation. It can be calculated by considering a molecule containing infinitely many blocks, picking any block in which we place the first monomer, summing over all possibilities for the block in which the second monomer is present, integrating over all positions of the monomers within their blocks, integrating over all possible block lengths, and adding a factor Q. As before, this factor will be cancelled by the factor $1/Q$ present in the normalization constant for ρ_s. The final result is

$$h^{(2)}_{AA} = \bar{n}\frac{\beta_z}{1-\alpha_z\beta_z}\frac{(1-\alpha_z)^2}{z^2}\,, \tag{A.13}$$

where β_z is the Laplace transform of the length distribution of the B-blocks. The second factor in equation (A.13) arises from the summation over the number of blocks that are present between the block containing i, and the block containing j, while the third factor is due to the integration over all possible positions of the monomers within their blocks. Adding the two contributions together we find

$$\frac{h_{AA}}{\bar{n}} = -\frac{(1-\alpha_z)(1-\beta_z)}{(1-\alpha_z\beta_z)\,z^2} + \frac{f}{z}\,. \tag{A.14}$$

The expression for h_{BB} can now be found by substituting $f \to 1-f$. Finally, we have to find expressions for h_{AB} and h_{BA}. In fact, these expressions turn out to be identical in the limit $Q \to \infty$. This is due to the fact that the molecule type $s_1 = \{n_1, n_2, ..., n_Q; m_1, m_2, ..., m_Q\}$ gives the same contribution to h_{AB} as its mirror image $s_2 = \{n_Q, n_{Q-1}, ..., n_1; m_Q, m_{Q-1}, ..., m_1\}$ to h_{BA}, while they have the same frequency of occurrence in the melt. It follows from equation (A.8) that, $\mathtt{g}_{AB}$ like $\mathtt{g}_{AA}$ and $\mathtt{g}_{BB}$, is a real-valued function. We obtain

$$\frac{h_{AB}}{\bar{n}} = -\frac{(1-\alpha_z)(1-\beta_z)}{(1-\alpha_z\beta_z)\,z^2}\,. \tag{A.15}$$

The expression for the second-order vertex function can now be found by applying equations (A.8) and (A.4). It remains to find expressions for the Laplace transforms α_z and β_z of the probability distributions. For the Schultz-Zimm distribution, which is defined by

$$P_\alpha(n) = \frac{k^k e^{-kn/n_\alpha}\, n^{k-1}}{\Gamma(k) n_\alpha^k}\,, \qquad \Gamma(k) = \int_0^\infty \mathrm{d}n e^{-n} n^{k-1}\,, \tag{A.16}$$

we have

$$\alpha_z = \left(1 + \frac{fz}{k}\right)^{-k}\,, \tag{A.17}$$

$$\beta_z = \left(1 + \frac{(1-f)\,z}{k}\right)^{-k}\,, \tag{A.18}$$

where k, the inverse polydispersity, has been defined in equation (3). The expressions for α_z and β_z for the monodisperse distribution can be obtained by taking the limit $k \to \infty$, leading to

$$\alpha_z = e^{-fz}\,, \tag{A.19}$$

$$\beta_z = e^{-(1-f)z}\,. \tag{A.20}$$

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